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INTERIM REPORT ON PIC MINIMIZATION IN A RESEARCH COMBUSTOR

by

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This report covers the period of January-March 1985, and the work was completed as of March 31, 1985.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of initial experimentation into the formation of Products of Incomplete Combustion (PIC) under conditions of flame quenching (brought about by use of high excess air rates). The research was conducted at EPA's Center Hill Thermal Destruction Laboratory, and will be useful to the understanding of this PIC-formation phenomena.

For further information, please contact the Alternative Technologies Division/Thermal Destruction Branch of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

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CONTENTS

Disclaimer ii
Foreword iii
Abstract iv
Figures vi
Tables vii

1. Introduction 1
2. Experimental Equipment 1
3. Experimental Design 3
4. Results 6
   POHC Destruction & PIC Formation 6
   Incinerability Information 10
5. Conclusions 11
   POHC Destruction & PIC Formation 11
   Role of the EPA Thermal Destruction Laboratory in Hazardous Waste Incineration Research 11
6. Future Work 13

References 14

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FIGURES

Number		Page
1.	Turbulent Flame Reactor	2
2.	Tenax Sampling Train	4
3.	Continuous Monitors	5
4.	Carbon Monoxide Levels & DRE Values vs. Excess Air Levels	8
5.	Emission Levels of $C_2H_2Cl_4$ and C_2HCl_3 vs. Excess Air Levels	9

TABLES

Number		Page
1.	DRE Values and CO Levels vs. Excess Air Levels.....	7
2.	DREs for TCE and Tetrachloroethane When Both are Burned Separately as POHCs.....	10
3.	Comparison of Freon and Chlorobenzene DREs for Combustion in Mixtures and Separately.....	12

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INTRODUCTION

Although the Resource Conservation and Recovery Act regulations require 99.99% Destruction and Removal Efficiency (DRE) with respect to Principal Organic Hazardous Constituents (POHCs), those chemical contaminants within a hazardous waste stream that are burned by an incinerator, there is also a concern about Products of Incomplete Combustion (PICs). These latter compounds are formed even as the POHCs in the incinerator are destroyed. They can be more toxic than the original feed chemicals. Thus, under those unwanted combustion conditions which favor the formation of PICs, hazardous waste incineration may give rise to a potentially serious air pollution problem.

The purpose of the work described in this Interim Report is to identify certain sets of conditions under which PICs form or are more prevalant so that future work can focus on how and why they form and how to minimize their forming. Contained within this report is a description of the combustor and auxiliary equipment used to conduct the study, a description of the experiments conducted and a discussion of the results obtained followed by a discussion of the future implications of the work. The work described herein is only preliminary and is rather limited. All conclusions drawn from this work are tentative and subject to future verification. The research described in this report is the result of the first efforts of EPA's in-house staff to conduct experiments at the Thermal Destruction Laboratory at their Center Hill Facility in Cincinnati, Ohio.

EXPERIMENTAL EQUIPMENT

Figure 1 is a sketch of the Turbulent Flame Reactor (TFR) which was used to conduct the experimentation discussed in this report. The TFR is a water-jacketed, stainless steel reactor with a designed heat load of about 100,000 BTU/hr (1). Combustion air, supplied by a compressor, enters the TFR through an International Flame Research Foundation (IFRF) windbox designed with movable swirl vanes that allow for adjustment of the linear and angular momentum imparted to the incoming air and for control over the resulting flame shape and stability. Heptane, mixed with various chemicals

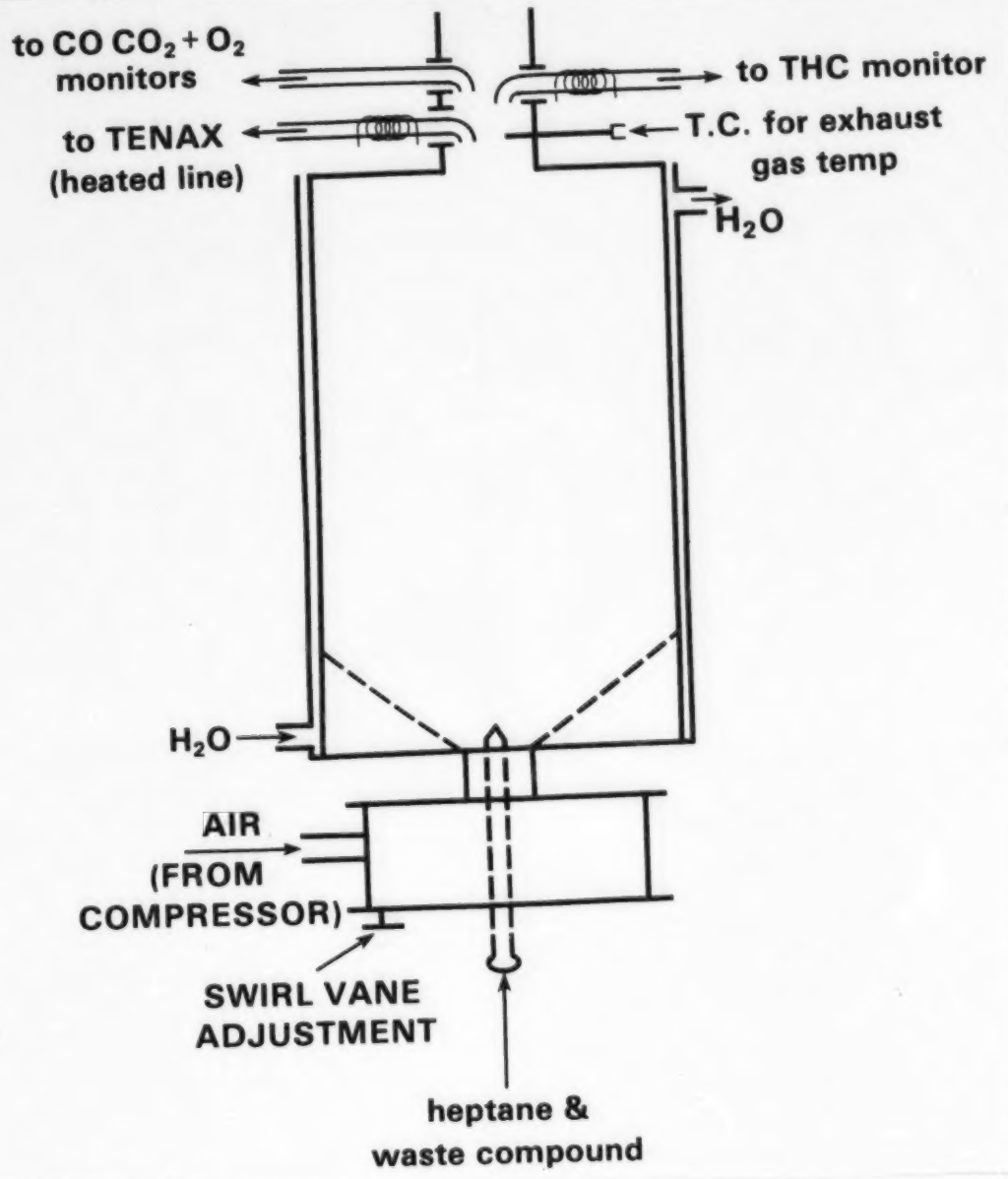

FIGURE 1. TURBULENT FLAME REACTOR

often chosen by industry as POHCs, is injected into the TFR through a Delavan pressure-atomizing nozzle inserted through the center of the IFRF windbox.

Tenax-filled sorbent traps are used to collect POHC and PIC emissions from the TFR. The Tenax sampling system used is shown in Figure 2. Sample gases enter through a 1/4" O.D. stainless steel probe which penetrates the TFR exhaust duct. They then pass through a heat-traced length of 1/4 O.D. teflon tubing where the temperature is kept at 130°C. Prior to leaving the heat-traced length of tubing, sample gases pass through a particulate filter. Heat tracing ends roughly six inches upstream of the Tenax trap in order to allow the gases to air cool from 130°C to about 20°C. The gases then pass through a Tenax trap containing 1.5 grams of Tenax-GC resin which adsorbs the volatile organic compounds in the exhaust gas sample. After that, the gases pass through a pump, a rotameter and a dry gas meter prior to being exhausted to the atmosphere. The Tenax trap samples were then analyzed by a gas chromatograph equipped with a Hall Detector.

To obtain continuous CO level readings, a Beckman Non-Dispersive Infra-Red (NDIR) monitor is used. A Beckman NDIR monitor continuously monitors CO_2 concentrations in the exhaust gas. Total Unburned Hydrocarbons (TUHC) are continuously monitored using a Beckman Flame Ionization Detector (FID) Total Hydrocarbon Monitor.

Figure 3 shows the continuous monitoring system used. Sample gas for CO, CO_2, and O_2 analysis is extracted from the TFR through a common sample line. Prior to entering the exhaust gas monitors, the sample gases pass through a particulate filter, a pump, and a laboratory gas drier containing calcium sulfate.

Finally, three "type K" thermocouples measure TFR exhaust gas temperature and sample gas temperatures in the heated and unheated portions of the sample line upstream of the Tenax trap.

EXPERIMENTAL DESIGN

The purpose of this experiment was to determine those operating regimes which allowed (1) incomplete burning of POHCs, and (2) formation of significant levels of PIC. A further objective was to compare the POHC and PIC levels thus produced with concentrations that result from flameout.

The above objectives were accomplished by burning five compounds (trichloroethylene (TCE), carbon tetrachloride, tetrachloroethane, chlorobenzene and Freon-113) in a series of five separate combustion tests. For each of the five tests, the compound of interest was present as a 2.0 mole percent solution in heptane in the combustor feed.

In a sixth test, Freon-113 and chlorobenzene were burned together to determine if there were any mixture effects which influenced POHC destruction and/or PIC formation. For this test, both Freon-113 and chlorobenzene were present at the same concentrations (two mole percent each) as when

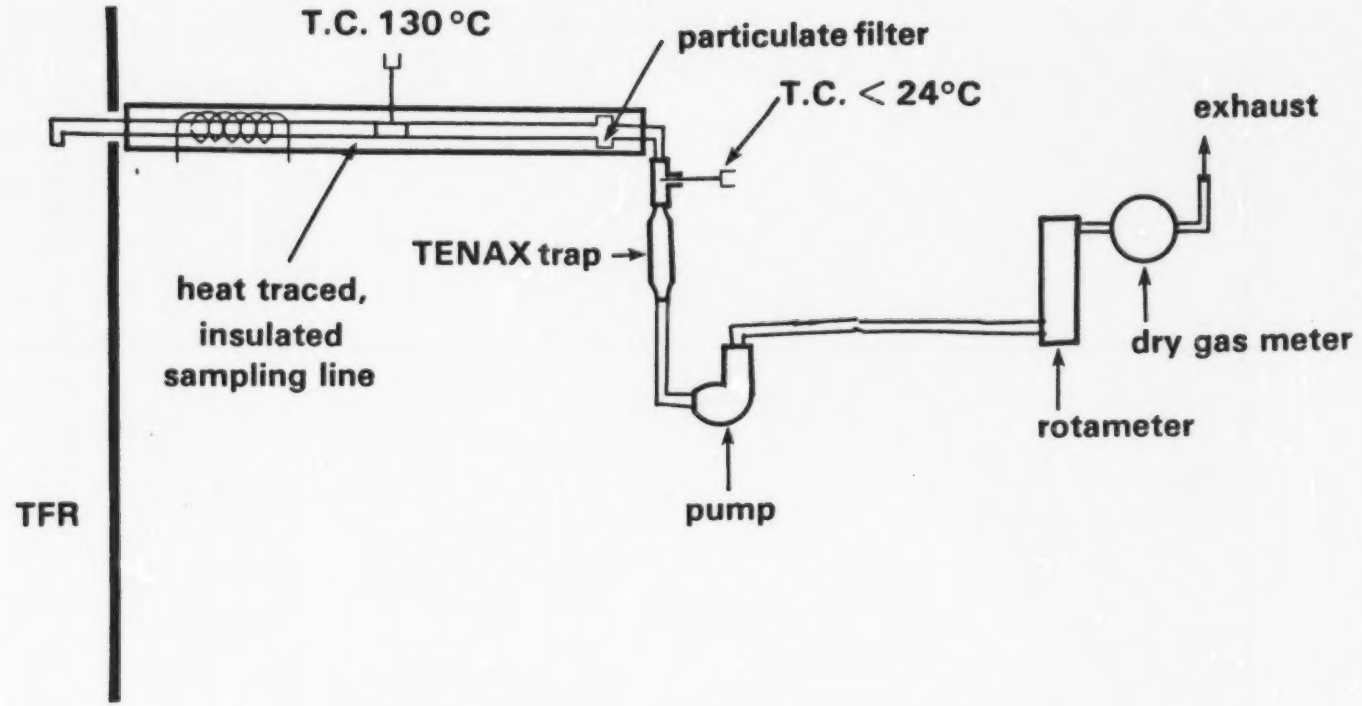

FIGURE 2. TENAX SAMPLING TRAIN

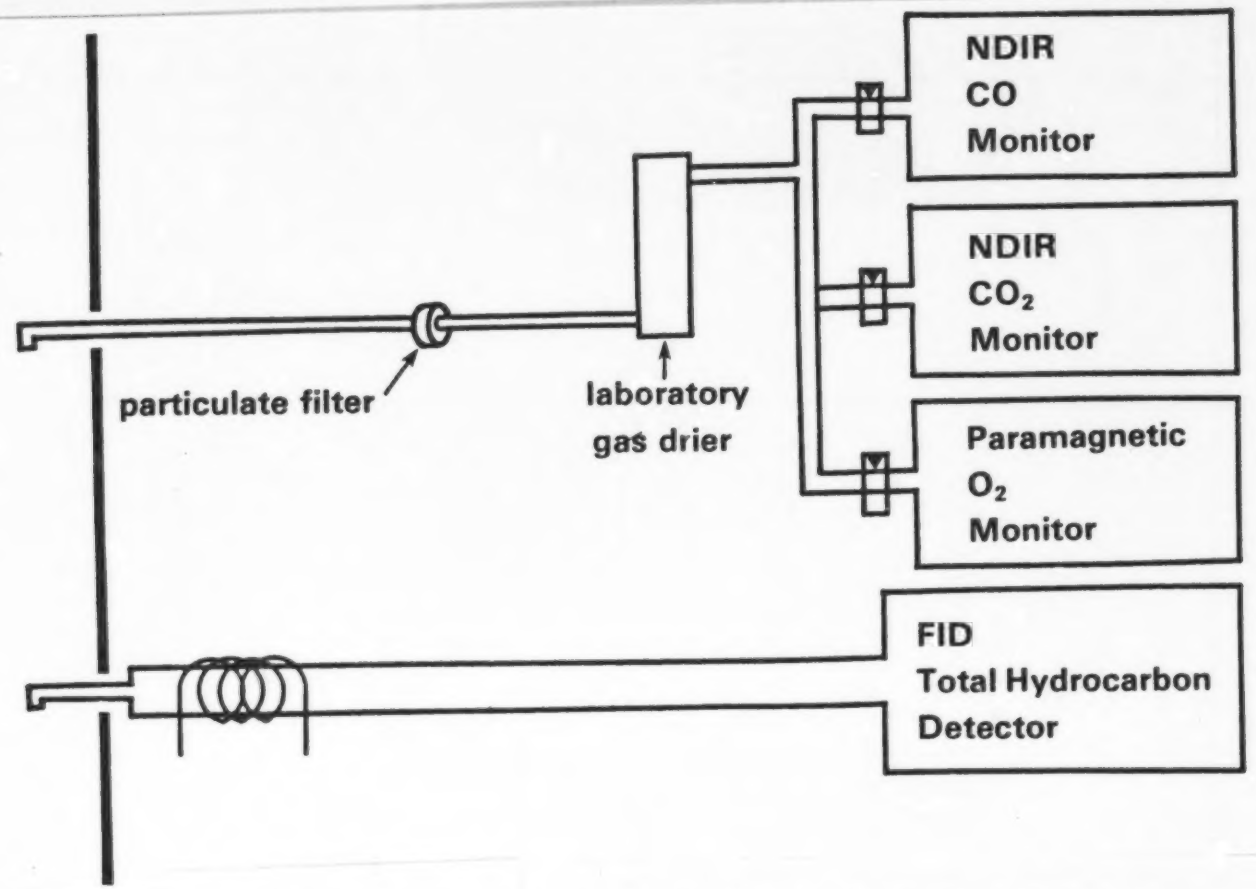

FIGURE 3. CONTINUOUS MONITORS

they were burned separately. This resulted in a total POHC concentration of four mole percent for this test.

In each test, the firing rate of heptane/POHC was held constant while the combustion air flow rate was varied to produce (CO) levels which spanned the range of observable values. At five or sometimes six different sets of operating conditions corresponding to five or six different CO levels, Tenax trap samples were taken for purposes of determining POHC destruction and PIC formation.

At one point during each test, the flame was purposely extinguished during a sampling run. Sampling continued. Theoretically, when the flame goes out, there should be a discharge of soot and PIC-laden exhaust gas from the reactor. The objective was to sample this emission and measure the unburned POHCs as well as to determine the types and levels of PICs produced during this "upset" condition. (It should be noted that all discharges from the TFR were scrubbed and filtered through an activated carbon filter to remove pollutants prior to discharge to the atmosphere.)

RESULTS

The DREs achieved throughout this test series exceeded 99.99% in 62.5% of the tests. For the remaining tests, DRE exceeded 99.9% except for the three times (two of which were flameouts) in which the DRE was slightly less than 99.9%. Table 1 and Figure 4 summarize the DREs achieved.

POHC Destruction and PIC Formation: Even though the DREs achieved were high, there were still significant POHC and PIC emissions especially when the TFR was operated under high excess air conditions (greater than 170% theoretical air). These emissions did not differ significantly from those observed when the flame was deliberately extinguished. More importantly, in one case there were significant PIC emissions even under conditions that produced 99.99% POHC DRE. In the test burn of tetrachloroethane, greater than 99.99% DRE was achieved under almost all conditions. Yet Figure 5 shows that the emissions of the PIC trichloroethylene (TCE) are significant and, in fact, exceed those of tetrachloroethane. One possible explanation is that not all of the POHC is completely combusted. Instead, tetrachloroethane is converted to the stable intermediate trichloroethylene during the combustion process. The temperature drop brought about with high levels of (cold) combustion air apparently quenched the combustion reaction of tetrachloroethane prior to completion. Trichloroethylene, an apparently stable intermediate of the above reactions, was emitted as a primary PIC. This result is not unusual. Researchers at the University of Dayton Research Institute have shown that tetrachloroethylene is a very thermally stable intermediate in the combustion of chloroform (2). Therefore, it is conceivable that trichloroethylene is also quite stable. If this is a correct assumption, further quenching, with still higher levels of cold combustion air, would tend to increase PIC (TCE) emissions. This indeed, was observed.

Not only was trichloroethylene a significant PIC of tetrachloroethane, but TCE was also a hard-to-destroy POHC. TCE was burned separately in a

Table 1. DRE Values and CO Levels vs. Excess Air Levels

Average CO Level	1000 ppm	300	200	300	400	500	800	1000	
Chlorobenzene and Freon	99.76* 99.998*	99.997 99.99	99.98 99.997		99.99 99.996			99.96 99.991	
Freon	99.998*	NA	99.992				99.994	99.996	
Chlorobenzene		99.994	99.99			99.98		99.76	99.92*
Tetrachloroethane	>99.999	99.992		>99.999		99.995		99.991* 99.97	
CCl_4	99.98	NA			>99.999		99.88	NA*	
TCE	99.994		99.98	99.97	99.78*				
% Theoretical Air	110	120	130	140	150	160	170	180	190	200	240

* - Flameout
NA - Not Available

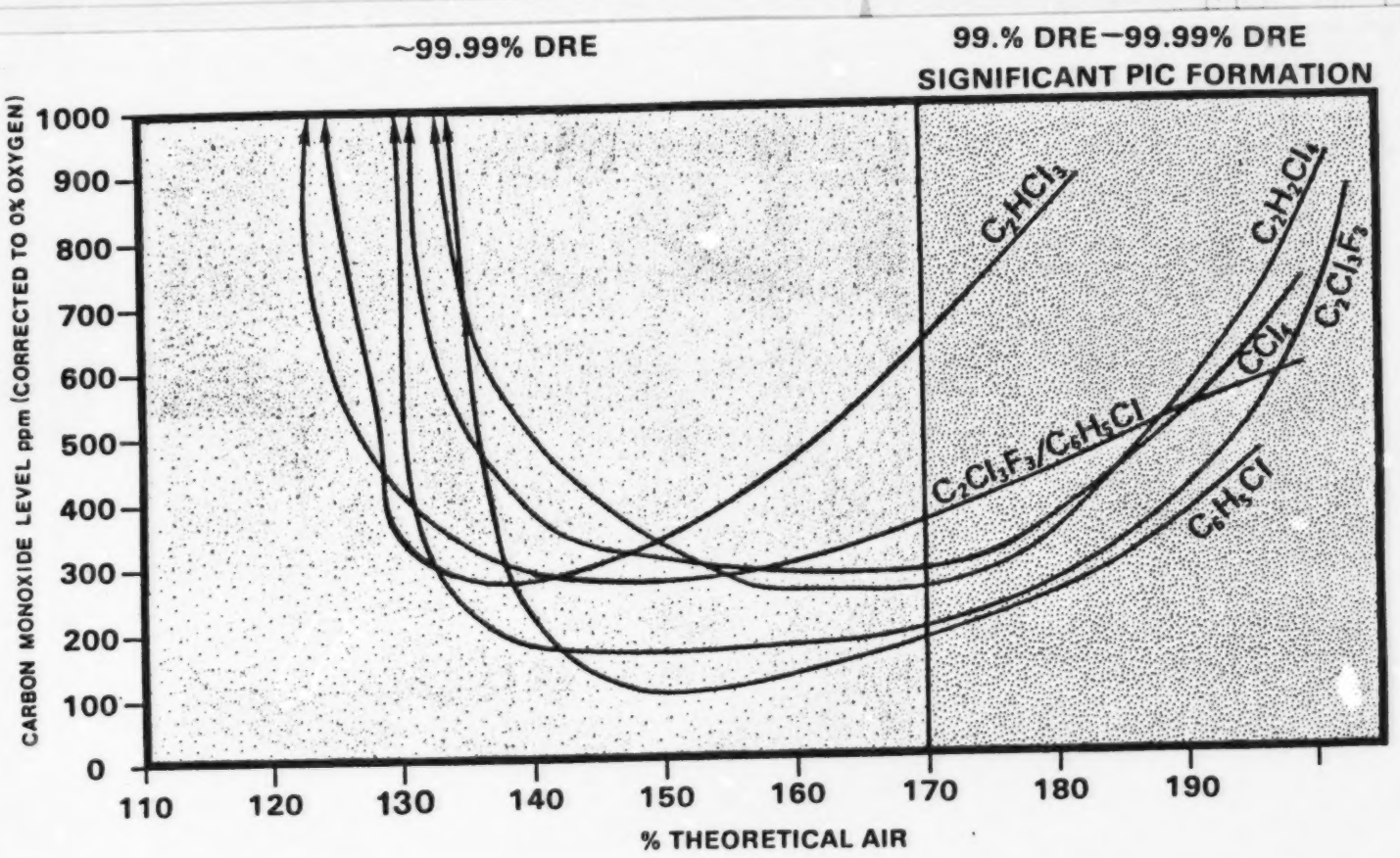

FIGURE 4. CARBON MONOXIDE LEVEL VS. EXCESS AIR AND DRE

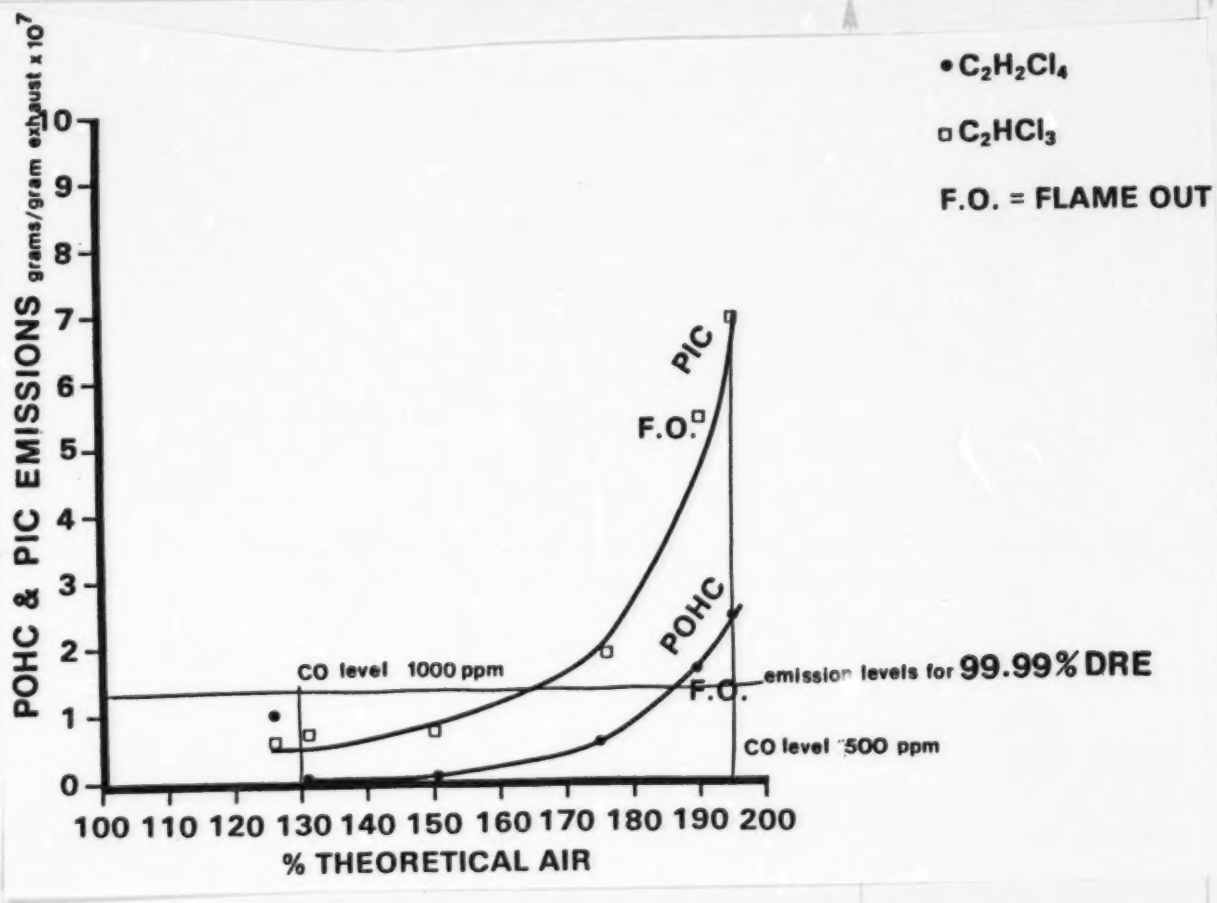

FIGURE 5. EMISSION LEVELS OF $C_2H_2Cl_4$ AND C_2HCl_3 VS. EXCESS AIR LEVEL

different test burn. DREs for TCE in this test are significantly lower than those for the test burn of tetrachloroethane as shown in Table 2. Further, the emission level of TCE in the test in which TCE was a POHC are roughly similar to the emission levels of TCE in the test in which TCE was a PIC. This suggests that POHC destruction and PIC formation are as much a function of the chemical being combusted as they are of incinerator operating conditions. Some compounds decompose easily, some do not. Thermally stable compounds will be hard to destroy whether they are present in the combustor as POHCs or PICs.

Table 2. DREs for TCE and Tetrachloroethane When Burned Separately as POHCs

TCE		.99994		.9998		.9997	.9978	F.O.		
									.99991	F.O.
Tetrachloroethane		>.99999	.99992	>.99999			.99995		.9997	
% Theoretical Air	110	120	130	140	150	160	170	180	190	200

F.O. = Flame Out

Incinerability Information: Another interesting observation about the TCE and tetrachloroethane DREs is that the results observed were totally unexpected based on the criterion commonly used to predict incinerability. Heat of combustion is the criterion most commonly used to estimate which compound would be hardest to decompose for purposes of writing hazardous waste incinerator operating permits. Compounds with lower heats of combustion are considered harder to burn. TCE's published heat of combustion is 1.74 kcal/gram whereas it is 1.39 for tetrachloroethane (3,4). Additionally, tetrachloroethane is more highly chlorinated than TCE and, therefore, it is commonly assumed to be harder to decompose, based on both criteria Results from these two test burns, however, point to a completely different conclusion. Other researchers have previously shown (5) that neither heat of combustion nor degree of chlorination correlates with the "incinerability" of a particular POHC. These results raise additional doubts regarding conventional "incinerability" criteria.

The dichotomy between "incinerability" predictions based on heat of combustion and degree of chlorination and DREs achieved in the laboratory was further illustrated by another set of tests, this time using chlorobenzene and Freon-113. In two tests, chlorobenzene and Freon-113 were combusted separately in heptane. In a third test, both Freon-113 and chlorobenzene were mixed together and combusted in heptane. Table 3 shows the DREs achieved for all three tests. The DREs for Freon-113 are

consistently higher than those for chlorobenzene even though Freon-113 is much more highly halogenated than chlorobenzene and is considered to be non-flammable.

The data seem to indicate that chlorobenzene is a much more stable compound than Freon-113 in spite of the fact that the opposite result was anticipated based on commonly used "incinerability" ranking criteria.

CONCLUSIONS

POHC Destruction and PIC Formation:

Fuel-lean combustion resulted in the highest levels of PICs and unburned POHCs. Emission levels of PICs and POHCs increased with increasing excess air levels. One explanation for this trend is that the temperature drop brought about by flooding the TFR with excess cold combustion air quenched the combustion reactions before they could reach completion. Stable combustion intermediates present when the reaction was quenched (either POHCs or PICs) were emitted in the discharge.

POHC and PIC levels produced under relatively fuel-rich combustion conditions were consistently low even though elevated carbon monoxide levels indicated that combustion conditions were poor. Even though the POHCs were apparently destroyed, it is conceivable that PICs may still be forming under these conditions. The PICs produced under relatively fuel-rich conditions could possibly be different than those produced under fuel-lean conditions and perhaps were not detectable using the methods and equipment used to analyze the samples generated during this study.

Types and amounts of PICs produced during flameouts were not appreciably different from those produced during fuel-lean operation. This is significant. Flameouts are momentary upsets which result in the production of a finite amount of POHC- and PIC-laden exhaust gas. Excessively fuel-lean combustion, however, often results in a stable though inefficient flame which can emit POHC- and PIC-laden gases for hours.

In two cases, these experiments have identified hard-to-burn POHCs that contradict previous expectations of incinerability based on heats of combustion and degree of halogenation. On the basis of the limited data gathered in these tests, no conclusions can be drawn regarding the setting of potentially new criteria for choosing POHCs and predicting which PICs can form under a particular set of combustion conditions. Yet these results and those of other researchers in the field, may be the basis for developing a more accurate way of identifying "hard-to-burn" POHCs and predicting PIC formation.

Role of the EPA Thermal Destruction Laboratory in Hazardous Waste Incineration Research: The conclusions above are not only valuable in determining useful areas for future research, they are also useful in determining how the TFR and also the rest of the EPA-Cincinnati Thermal Destruction Laboratory can contribute to the hazardous waste incineration

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Table 3. Comparison of Freon and Chlorobenzene DREs for Combustion in Mixtures and Separately

% Theoretical Air	110	120	130	140	150	160	170	180	190	200	240
CO Level		1000 ppm		300	200	300	400	500	800		1000
Test 4 Chlorobenzene (alone)			99.994		99.99			99.98		99.76	99.92*
Test 5 Freon (alone)	99.998		NA		99.992				99.994	99.996	
Test 6 Chlorobenzene (mixed)		99.76*	99.997		99.98		99.99		99.96		
Freon (mixed)		99.998*	99.99		99.997		99.996		99.991		

* - Flameout
NA - Not Available

research efforts underway nationwide.

One problem that can perhaps be partially treated by the TFR is that of finding a better way of selecting POHCs. As has been shown in this report, heats of combustion and the degree of halogenation of a compound do not always indicate how hard it may be to destroy a particular POHC. By using the TFR in experiments such as the ones outlined in this report, it would be possible to better define what POHCs are hard-to-burn and therefore should be chosen for compliance testing. These experiments can be used to substantiate the data gathered by the non-flame Thermal Destruction Unit-Gas Chromatograph on POHC destruction and PIC formation. This data could also be used to design experiments in larger units (for example, at the EPA Combustion Research Facility in Pine Bluff, Arkansas) that would further validate original hypotheses.

As an extension of the above work, the TFR and the other combustion units at the EPA Center Hill Facility could be used to test proposed tracers and other suggested real-time DRE indicators. For some time now, researchers have been looking for some means to immediately warn of the onset of incinerator performance deterioration and resulting drop in DRE. Carbon monoxide has been considered a likely real-time DRE indicator and many researchers have been trying to develop correlations between DRE and carbon monoxide level in incinerator exhaust gas. Similar work is being done to investigate the usefulness of other combustion intermediates such as total organic chloride and tracers like Freon-113. With the small combustors at the Center Hill Facility, short test times and wide operating flexibility allow for rapid testing of these proposed DRE indicators.

FUTURE WORK

As a follow-up to this Interim Report, future research on the TFR will be aimed toward validating the tentative conclusions presented herein. Tests will also be conducted to determine what (if any) PICs form under relatively fuel-rich conditions. The search for new POHCs and PICs will be expanded and potential DRE indicators will be investigated by testing under a variety of combustion conditions. A major objective is to develop an understanding for why particular chemicals do not burn well in combustors.

The results from the TFR will be used to plan tests for our refractory-lined combustor, which will be used to test the influence of the downstream heat retention of a refractory-lined chamber on the preliminary conclusions reached in this TFR research.

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